Acylation of Cotton Fabric with Isopropenyl Stearate[1]

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ABSTRACT

Cellulose fabric is rapidly made water-repellent by direct acylation with isopropenyl stearate, which is representative of isopropenyl esters of long-chain fatty acids. The esterification produced a material with minor change in tensile strength. Acylation by isopropenyl stearate (IPS) was accomplished by transfer of reagent to cloth followed by heat-curing in an acid-catalyzed reaction. The low levels of catalyst (0.05% by weight of IPS), short curing periods (7–60 s), and low heating temperatures (~180°C) provided conditions for chemical incorporation of a fatty acid at low levels of substitution (DS < 0.001).

Introduction

Current methods of acylation for grafting long-chain substituents onto cotton cellulose suffer many disadvantages and impracticalities. Cotton is strongly resistant to direct reaction with long-chain fatty acids, and the fabric may be severely degraded when reaction is forced in the presence of catalysts. In the past, acylations of cotton have been achieved principally by a) reaction with an acid chloride in dimethyl formamide (DMF) solvent [10]; b) treatment with a benzene solution of the fatty acid and trifluoroacetic acid anhydride [3]; c) the classic Karrer method in which the cotton is first padded with aqueous sodium hydroxide and is then immersed in a carbon tetrachloride solution of an acid chloride [8]; and d) reaction of dry sodium cellulosate with an acid chloride in DMF [2]. The effects of the nature, including the chain length, of the fatty acid upon the physical properties of cotton cellulose have been described [1, 7, 11, 12].

For several years members of our laboratory have studied the chemical reactions of enol esters, especially isopropenyl stearate (IPS) and have found these compounds to be excellent acylating agents [5, 9, 14–19]. In the presence of catalytic amounts of strong acids, *e.g.*, *p*-toluenesulfonic acid monohydrate (PTSA), isopropenyl esters react with active hydrogen compounds such as alcohols, amines, amides, imines, and others to acylate them. In this respect, isopropenyl esters are similar to, but more reactive than, acid chlorides.

Acylation with isopropenyl esters has the distinctive feature of evolving acetone co-product (Equation 1).

$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{R{-}C}}{-}\mathrm{O}{-}\underset{\substack{| \\ \mathrm{CH_3}}}{\mathrm{C}}{=}\mathrm{CH_2} + \mathrm{R'OH} \xrightarrow{\mathrm{H^+}} \underset{\substack{\| \\ \mathrm{O}}}{\mathrm{R{-}C}}{-}\mathrm{OR'} + \mathrm{CH_3}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{CH_3} \qquad (1)$$

This method, in which a minor amount of acid catalyst is necessary for reaction, contrasts to other acylation methods in which stoichiometric or larger amounts of acids or bases are present or formed and must be neutralized. Isopropenyl esters can be prepared from fatty acids and methyl acetylene in high yield and purity [18], and an excellent continuous process for their preparation has been described [6]. Isopropenyl stearate has decided advantages as an acylating agent over stearoyl chloride because: it is readily prepared free of phosphorus or sulfur impurities, it is a cyrstalline solid that is highly stable on storage, and in use it gives rise only to neutral, volatile acetone rather than the nonvolatile, corrosive chloride salts usually associated with acylations involving acid chlorides. Furthermore, the cost of production of IPS is expected to be competitive [21] with that of acid chlorides.

In view of the advantages of IPS, we have examined its reaction with cotton cloth to test its effectiveness in imparting water-repellency. We also examined the tensile strength of the treated material in order to obtain a measure of the effect of the treatment on mechanical properties.

Experimental

MATERIALS. Isopropenyl stearate was prepared from commercial grade stearic acid [stearic acid (89%), palmitic acid (9%), and remaining homologues (2%)] by the reported method [18]. Solvents were analytical

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reagent grade. All acid catalysts, with the exception of partially dehydrated phosphoric acid, were used as received without further purification. Partially dehydrated phosphoric acid was prepared by addition of P_2O_5 (395 mg) to 85% H_3PO_4 (1.0 g).

All fabric samples used in this study were air-equilibrated. The samples were taken from an 80 × 80 cotton print cloth weighing 108.5 g/m² that had been desized, scoured, bleached, and soured.

Fabric Treatment. Cloth samples 20-cm square were chosen from the bolt and assigned for treatment on the basis of randomized blocks. Since tensile strength of samples from a bolt of cloth may vary as much as 10%, a randomized block design was used in order to minimize the effect of this variation on the results. Each block consisted of ten pieces of cloth, which were randomly assigned to the two controls and the eight specific treatment combinations of curing temperature, reaction time, and acid-catalyst concentration (each of these three factors being present at two levels).

Neat Application of IPS. The cloths were placed on a Pyroceram[4] plate and covered by a neat melt of IPS containing PTSA or other acid catalyst, at predetermined levels. Heating to effect chemical reaction was accomplished by direct application of a heated flatiron to the treated material. The temperature of the iron was closely controlled with a thermostat contained in the sole plate. Each side of the cloth was separately cured at the given temperature and time interval. Since the area of the treated cloth was approximately twice the area of the iron, the latter was moved over the surface of the sample for twice the period indicated, so that each spot on the cloth received heating for the prescribed period. The other side of the sample was then heated in a similar manner and for the same period. The brief intervals of exposure to the high temperature of the iron were insufficient to cause thermal or oxidative damage to the cellulosic material. Alternatively, curing was accomplished by pinning the "wetted" cloth to a wooden frame, air-drying the cloth, and then heating the cloth in an oven for the prescribed period. After being cured, the cloth was extracted in a Soxhlet extractor with diethyl ether for removal of unreacted IPS and catalyst.

Solvent Application of IPS. The test fabric was dipped into a benzene[5] solution of IPS containing the acid catalyst, excess solvent was squeezed from the cloth in a wringer, and the sample was air-dried. Curing was accomplished either by ironing or by placing the sample in a preheated oven as described above. The extraction of excess reagent and catalyst was carried out as described above.

Determination of Degree of Substitution. A method for the determination and identification of chemically bound fatty acids present on partially esterified cotton has been reported [4]. A faster microtechnique to accomplish this determination was devised and is still being evaluated. This method is reported in an accompanying paper [20].

Physical Testing Procedures. Water repellency was determined by the AATCC Test Method 22-1971. A sample of a commercially available Impregnole-finished white cotton duck 325 g/m² with a water repellency of 100 was useful for comparative purposes. Tensile strengths and percent elongation were determined by the ASTM Test Method D-1682-64(70) on cloth strips (gauge length 25 mm) on an Instron Tester Model No. TT-B. On most of the sample cloth strips, tensile strength was determined separately in the warp (W) and fill (F) directions.

Results and Discussion

In the past, partial esterification of cellulose has been accomplished by causing a solution of the acylating agent to react with the substrate. The strategy of the current study was to apply the acylating agent, mixed with acid catalyst, to the cellulose, either by neat application or by deposition from solution, to bring the two reactants into physical contact. Only then was heat applied briefly to effect chemical reaction. Our acylating agent was isopropenyl stearate (IPS), and our acid catalyst was, in most cases, *p*-toluenesulfonic acid monohydrate (PTSA).

The goal of this work was the testing of IPS as an acylating agent that provides an overall improvement in the properties of the cellulosic material treated. We hoped to achieve a substantial increase in water-repellency with little or no loss in tensile strength. We are aware that the degree of water-repellency desired and the loss of tensile strength that can be tolerated depend on the specific application for which the treated material is intended.

Neat application of IPS plus catalyst has the advantage that the surface of the material to be treated is saturated without noticeable swelling of the cellulose fiber. An additional advantage is that the pool of melted IPS apparently facilitates heat transfer and gives a more rapid reaction of the fiber surface with IPS. A disadvantage of the neat method of application is that the large excess of unreacted IPS and catalyst must be removed, either by solvent extraction or by other means. Removal is necessary because the

[4] Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

[5] The Occupational Safety and Health Administration, under Standard 29 CFR 1910.1000 Table Z-2, has stated that benzene is a carcinogen.

excess acid catalyst can be expected in time to degrade the cellulose fiber. Furthermore, stability studies of IPS at our laboratory have indicated that, while the ester itself is perfectly stable at room temperature for years, IPS containing PTSA has a tendency to degrade with time, one product being stearic anhydride. The rate of degradation of IPS is a function of the concentration of PTSA dissolved in it.

Exploratory experiments of the neat application of IPS and PTSA indicated that important parameters were the temperature at which the treated cloth was heated, the period of heating, and the concentration of the catalyst in the IPS. For instance, it was noted that at 130°C little acylation occurred even on prolonged heating, while at 270°C, and more so at 320°C, the physical properties of the cloth declined because of scorching.

In order to examine the three parameters systematically, we designed (see Fabric Treatment) a set of experiments (using randomized blocks) which led to the investigation of the factors at the levels indicated in Table I. We analyzed the data by computing the difference in tensile strength between each treatment and the control within each block and performing an analysis of variance on these differences. The treatment that resulted in excellent water-repellency combined with a significant ($p = 0.05$) retention in tensile strength (W-direction) and an essentially unaltered tensile strength (F-direction) was the combination of ironing at 180°C for 4 s with 0.05% PTSA.

Solution application of IPS, containing acid catalyst at the 0.05 weight percent level, was also investigated. Solution application has the advantages that a minimum of acylating agent is recycled and that the amount of acylating agent applied is more readily controlled. Disadvantages of solution application are that solvent vapors need to be controlled for worker protection and that multiple applications may be required to deposit the desired amount of acylating agents.

Our studies were limited to the use of benzene as a solvent, because both IPS and PTSA are soluble in it. In the light of recent information regarding the adverse health effects of benzene, another solvent such as toluene would be preferable. Criteria for useful solvents are stability toward acylation by IPS and toward deterioration by acid catalysts, good solubilizing action for IPS and the catalyst, proper volatility, and inertness toward cellulose.

A number of acids in addition to PTSA were investigated for their ability to catalyze the IPS acylation of cellulose without adversely affecting the physical properties of the latter. Only 2-naphthalenesulfonic acid and, to a lesser extent, partially dehydrated phosphoric acid were effective in conjunction with IPS in imparting water-repellency to cotton cloth when deposited from a melt or from solution. Formic acid, trichloroacetic acid, and trifluoroacetic acid did not consistently catalyze IPS acylation under the conditions used, and the treated cloths experienced no change in tensile strength or water-repellency as a result of treatment.

In a randomized block experiment we examined the effects of the nature of the catalyst (β-naphthalenesulfonic acid *vs.* PTSA *vs.* partially dehydrated phosphoric acid), the IPS application method (neat *vs.* solution), and the method of curing (iron *vs.* oven). Response was measured in terms of water-repellency and change in warp tensile strength over that of the untreated cloth. All treatments were carried out in quadruplicate. We chose the randomized block design to minimize the effect of the variation (500–600 psi (3450–4150 kPa)) in warp tensile strength encountered in the bolt of untreated cloth on the conclusions (average warp tensile strength, 5200 psi (35 850 kPa)). Nevertheless, an analysis of variance carried out on the warp tensile strength data after treatment revealed that large variations among untreated samples within the same block decreased the significance of the results. Furthermore, since water-repellency and tensile strength are important measures of the success of the treatment, the consideration of tensile strengths alone failed to provide the desired information.

The data obtained in this experiment are shown in a condensed form in Table II. These and the raw experimental data (not included) indicate certain

TABLE I. Neat isopropenyl stearate acylation: effect of parameters on fabric properties.[a]

Temp, °C	PTSA,[b] %	Time, sec.	Warp Thickness, in.[c]	Warp Elongation-at-break, %	Warp Breaking strength, lb.[d]	Warp Tensile strength, psi[e]	Fill Thickness, in.[c]	Fill Elongation-at-break, %	Fill Breaking strength, lb.[d]	Fill Tensile strength, psi[e]	Water-repellency
Untreated cloth			0.00934	15	52	5560	0.00900	33	36	4015	0
180	0.005	4	0.00956	16	58	6090	0.00928	32	39	4225	0
210	0.005	4	0.00937	15	53	5700	0.00933	31	39	4125	0
180	0.05	4	0.00953	16	57	6005	0.00939	31	37	3950	100
210	0.05	4	0.00918	14	46	5005	0.00925	31	29	3085	100
180	0.005	7	0.00953	16	58	6055	0.00946	33	37	3830	0
210	0.005	7	0.00948	16	55	5825	0.00924	32	38	4095	50
180	0.05	7	0.00919	16	53	5810	0.00937	32	34	3625	100
210	0.05	7	0.00923	14	47	5885	0.00932	30	31	3300	100

[a] Treated samples: average of 3 samples; untreated control: average of 6 samples. [b] Percent by weight, *p*-toluenesulfonic acid. [c] To convert to SI units (mm), multiply by 25.4. [d] To convert to SI units (N), multiply by 4.448. [e] To convert to SI units kPa), multiply by 6.895.

TABLE II. Effect of several parameters on tensile strength and water-repellency.[a]

Catalyst	Application	Cure	TS, psi[b] Warp	Fill	WR[c]
Control[d]		Iron	5210	3700	0
		Oven	5190	3880	0
β-Napthalene-sulfonic acid	Neat	Iron	4900	3740	90
	Neat	Oven	4310	2960	80
	Solution[e]	Iron	5080	3600	70
	Solution[e]	Oven	5250	3820	70
p-Toluenesulfonic acid	Neat	Iron	4660	3420	90
	Neat	Oven	4800	3480	90
	Solution[e]	Iron	5520	3970	70
	Solution[e]	Oven	4720	3490	70
H_3PO_4/P_2O_5	Neat	Iron	4960	3470	90
	Neat	Oven	4040	3380	80
	Solution[e]	Iron	5340	4160	50
	Solution[e]	Oven	5400	3950	0

[a] Each value represents the average of four sample values.
[b] To convert to SI units (kPa), multiply by 6.895.
[c] Water-repellency (WR) measured by AATCC Test Method 22-1971.
[d] Untreated cloth; separate iron and oven controls used for statistical analysis.
[e] Solution in benzene solvent.

trends, although improved certainty of the relationships would require a considerably greater number of replicates. Overall, neat application appears to provide better water-repellency than the solution application procedure used in this experiment. Since sample-to-sample variations of 500–600 psi in tensile strength are common, most of the average tensile strength values seen in Table II are reasonably close to those of the untreated samples. However, since the tensile strengths of the samples treated by neat application are consistently below those of the untreated samples, as well as those treated by solution application, it appears that neat application does lower tensile strengths somewhat. Solution application, on the other hand, results in tensile strengths that are sometimes higher and sometimes lower than the untreated samples. The raw data indicate that better water-repellencies are consistently associated with slightly lower tensile strengths. Thus it appears that attainment of good water-repellency is accompanied by a slight lowering of fabric strength, regardless of the method of application.

Data on the manner of curing indicate that ironing and oven-drying are equally acceptable. Both methods seem adequate in causing the acylation reaction to proceed to the same extent. There is no indication of sensitivity toward heating time, although our other experiments demonstrated that brief heating periods are preferable and good temperature control is essential.

β-Naphthalenesulfonic acid and PTSA were satisfactory catalysts, although the latter appeared to give slightly better water-repellency. Partially dehydrated phosphoric acid was somewhat inferior to both sulfonic acids, especially in solution application, and gave lower water-repellencies. Deterioration of fabric strength seemed somewhat more pronounced when partially dehydrated phosphoric acid was the catalyst in neat application.

Attempts to measure the amount of acylation by weighing cloth samples before and after treatment encountered difficulties. The weights of air-equilibrated samples before and after treatment were the same within experimental error. It became apparent that water-repellency had been achieved by esterification of an unexpectedly small number of the available cellulose hydroxyl functions, so that the add-on could not be determined gravimetrically with confidence. It was therefore necessary to determine the degree of substitution (DS) by an alternative method.

In the present study DS's on the order of magnitude of 1×10^{-3} were attained. These were determined by saponification with methanolic or propanolic potassium hydroxide followed by isolation and glc determination of the isolated fatty acids [20]. The low DS indicates that only one out of every one thousand anhydroglucose units bears a substituent.

Cellulose esters of relatively low DS have been prepared by several methods of esterification. However, in a comparison of equivalent DS for a given cellulose ester, the esterification method has been shown to be a controlling factor in the resultant fabric properties [2]. The low DS in treated fabric with essentially unchanged dimensional properties indicates that esterification was probably confined solely to the fiber surface, preserving the integrity of the intercrystalline regions. This result is in contrast to solvent-supported esterifications such as occur with acyl halides in DMF or pyridine solutions. In such liquid media, swelling of the fiber exposes the less accessible intercrystalline hydroxyl sites by disruption of intermolecular hydrogen-bonding interactions, thus facilitating chemical attack [13]. Under the conditions of the present study, fiber swelling does not appear to occur, and only surface hydroxyl groups seem to have been acylated.

The present study has demonstrated that IPS is a useful and convenient agent for the topical modification of cellulose products. The water-repellencies of the IPS-treated fabrics were generally comparable to that of a commercially available Impregnole-finished white cotton duck. No attempt has been made to develop an optimum treatment process, and alternative procedures are clearly available in the manner of application (*e.g.* spraying) or in the heat-curing method (*e.g.* heated rollers). Since the long-chain acyl groups are chemically combined with the cellulose, the treated materials are expected to retain their water-repellency upon exposure to organic solvents, as for instance during dry-cleaning, and may find application in situations where soil resistance is not demanded. Furthermore, the surface acylation may well render the treated materials resistant to microbiological attack.

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